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Estuaries as hot spots of mercury methylation: the influences of sulfide, salinity, and organic matter

Methylmercury is a known teratogen, and causes sensory and nervous system damage in people exposed pre- or post-natally. It may cross the blood-brain barrier to reach the fetus, then oxidizes to inorganic mercury which binds to the sulfhydryl groups on proteins, especially interrupting the cell division of nerve cells. In adults, toxicity includes numbness, vision and hearing loss, tremors, the inability to concentrate, and potentially coma and death (Klaassen and Watkins 2003; Hodgon and Levi 1997). The half life of methylmercury is 2 to 3 months in humans (Young 2001; IPCS 1990) and in fish (Kramer and Neidhart 1974).

Global mercury cycle

Methylmercury is a product of mercury transformations. Elemental mercury is volatile with a half life in the atmosphere of about a year, and there is an estimated pool of atmospheric mercury of 25Mmol (Morel et al 1998). Atmospheric mercury is distributed globally until it returns to earth as dry deposition or oxidizes to the water soluble Hg(II) ion and returns via rain, snow and fog (Carpi 1997). Atmospheric oxidation generally occurs via ozone in fog and clouds, but may also occur by radical hydroxyl ions, HClO, and HSO_3^- (Morel et al 1998).

An estimated 54 Mmol of mercury is thought to be in the surface ocean; some Hg(II) will photoreduce in surface waters, but 70 - 90% will remain in the Hg-ligand form (Morel et al 1998). Above oceans and estuaries, Hg(II) will primarily form as $HgBr_2$ and $HgCl_2$. Mercuric (II) chloride is highly soluble in water compared to elemental mercury (Table 1) and will preferentially partition into and migrate with water, rather than air. With a K_{ow} of 3.3 (Table 2), $HgCl_2$ is soluble in water and fat, and will easily move across the cell membranes of aquatic organisms. Because mercury is toxic to bacteria as well as to higher life, aquatic bacteria transform $HgCl_2$ and efflux it before the molecule oxidizes and harms cell proteins (Figure 1). Many reduce $HgCl_2$ back to Hg^0 and allow it to volatilize; most mercury in the ocean goes through cycles of volatilization, precipitation, and re-emission, with only an estimated 1-2 pM reaching deep sediments (Morel et al 1998). If elemental H_2S is present as Hg^0 is released, though, as is the case near sulfate-reducing bacteria (SRBs), then Hg will preferentially precipitate as HgS rather than volatilize (Lamborg et al 2004).

When mercury salts cross the membranes of SRBs, the salt is methylated to the monomethylmercury (MeHg) form, such that $HgCl_2$ becomes CH_3HgCl, $Hg(OH)_2$ becomes CH_3HgOH, and it has been proposed that $Hg(HS)_2$ may become CH_3HgHS (Morel et al 1998; Compeau and Bartha 1987). Although SRBs are not the only bacteria that methylate mercury, they are the primary group (Macalady et al 2000; Compeau and Bartha 1987). Once MeHg is released and diffuses into the water, it will partition into fat when ingested. In this way it bioaccumulates, such that phytoplankton may have 300,000 times more mercury than surrounding water, and the bioconcentration factor in fish may be 10,000 (IPCS 1990) up to 3 million (EPRI 2004).

Mercury poisoning

There are only two sites where mercury poisoning through fish consumption has been documented: Kyushu, Japan on Minimata Bay, and Niigata, Japan on the Agano River (Figure 2). In both cases, mercury was a catalyst in industrial acetaldehyde production, and waste was dumped into water bodies. Commercial fishermen and their families exhibited neurological symptoms such as paraesthesias (numbness, tingling, burning of the skin), tremors, spontaneous emotional displays, and vision and hearing loss (Hodgson and Levi 1997). Some children born into fishing families had severe mental and physical abnormalities. Nearly 20,000 people in Mini-

Table 1. Physical properties of Hg and some Hg species at 25C

Species	density (g/cm^3)	vapor pressure (mm Hg)	solubility (g/L)
Hg^0	13.5[a]	0.002[a]	6×10^{-7}[a]
CH_3HgCl	4.06[a]	0.0085[a]	0.020[b]
$HgCl_2$	5.6[a]	1 at 136C[a]	73[a]
$Hg(OH)_2$	--	--	--

Table 2. Physical properties of Hg and some Hg species at 20C (Hg^0), 25C (Hg species)

Species	log K_H [air]/[water]	log K_{ow} [oct]/[water]	log K_D [soil]/[water]
Hg^0	-0.5[c]	6.0[a]	--
CH_3HgCl	-4.7[c]	1.7[d]	-2[e]
$HgCl_2$	-7.5[c]	3.3[f]	--
$Hg(OH)_2$	-5.4[c]	0.5[f]	

references for both tables are as follows: a) ATSDR 1999 b) Ammons et al 1977 c) Lindqvist and Rodhe 1985 d) Morel et al 1998 e) Heyes et al 2004 f) Benoit 2000, at 10^{-4}M [Cl-]

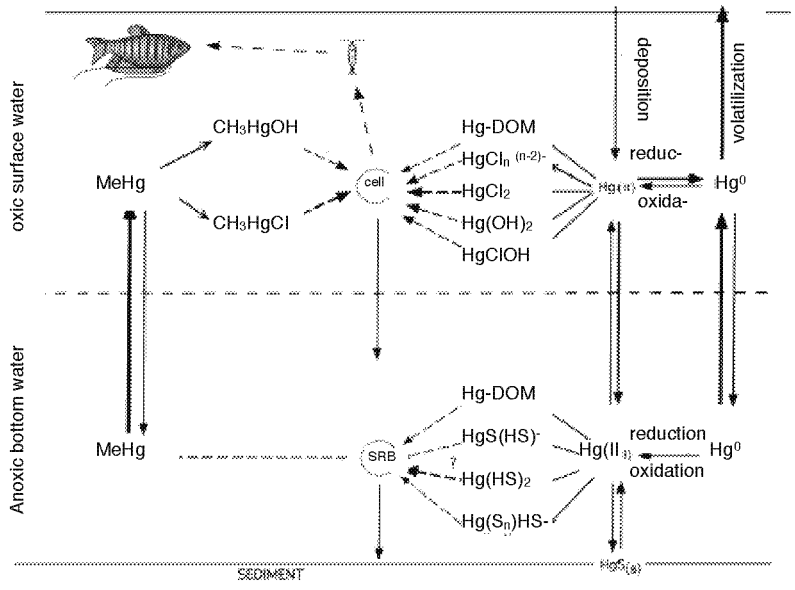

Figure 1. Aquatic mercury cycling (from Morel et al 1998)

mata have applied for "recognition" as victims of mercury poisoning, although only 3,000 have been certified; all 3,000 have neurological damage (Meyers et al 2004). Because of the publicity surrounding Minimata disease, doctors in Niigata quickly recognized the symptoms when mercury poisoning occurred there in the 1960s, about ten years after the Minimata incident, and took steps to reduce exposure. Due to the public health campaign, only one case of prenatal exposure was documented in Niigata, with the mother's hair measuring 293 ppm mercury. The primary effect in Niigata was vision damage (Meyers et al 2004).

These dramatic episodes caused countries around the world to become aware of methylmercury issues. Fish advisories due to mercury are found in all but 6 states in the US. As of 2004, 20 states had advisories that included *all* lakes; 18 also included all rivers (USEPA 2006). Fish are considered safe with 0.5 to 1 ppm (Morel et al 1998; IPCS 1990), compared to fish and shellfish at Minimata and Niigata with 40 ppm (Meyers et al 2004). Fish tissue of non-predatory ocean fish range from 0.005 to 0.25 ppm, and of predatory fish such as tuna and shark are generally 0.3 to 1.8 ppm (IPCS 1990).

Sources of mercury

Volcanoes, wildfires, soils, and degassing of the Earth's crust may emit 3,000 to 6,500 tons of mercury per year, with anthropogenic sources such as fossil fuel combustion, smelting, and incineration contributing another estimated 2,200 to 3,300 tons per year (IPCS 1990). While these numbers have significant levels of uncertainty, it is clear that despite regulations that have reduced anthropogenic inputs to the atmosphere up to 50% in some areas, a consequent decline in methylmercury in fish and shellfish has not been seen (Sunderland et al 2004). The concentration of methylmercury in aquatic organisms in pristine systems can be as high or higher than those living in polluted systems, and it is apparent in many studies that the concentration of methylmercury is *not* related to the concentration of Hg(II) (Lambertson and Nilsson 2006; Heyes et al 2004; Macalady et al 2000) or total mercury (Lambertson and Nilsson 2006; Stoichev et al 2004). Stable isotope measurements in Ontario found that while 30 to 40% of newly deposited atmospheric mercury is re-emitted from lakes, only 10 to 15% is re-emitted from wetlands, indicating that wetlands provide conditions for methylation that keeps mercury in the system (Biogeochemistry class notes re Metaalicus project).

Methylmercury in water bodies

Given that mercury is available to all terrestrial and aquatic systems through atmospheric deposition, what conditions then promote methylation? Essentially there are two requirements: SRBs[1], and mercury in the form of a neutral species.

Pristine freshwater rivers and lakes generally have little sulfate, which SRBs require as an electron acceptor, therefore methylation is limited through limiting SRB growth. In addition, in freshwater oxygenated systems, SRBs have competition from other microbes, as the variety of electron acceptors supports diverse communities (Compeau and Bartha 1987). Oceans have unlimited sulfate and are rich in SRBs, but high sulfide levels limit methylation (Langer et al 2001), possibly by the formation of charged mercury-sulfide species such as $HgHS_2^-$ and through charged mercury-chloride species such as $HgCl_3^-$.

Estuaries are areas of high sulfate and low sulfide concentrations,

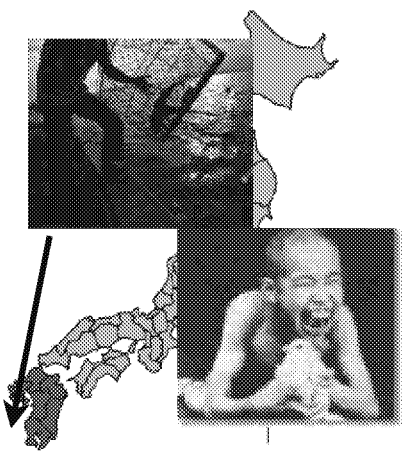

Figure 2. Minimata Bay in the Kyushu district of Japan Top: fisherman in Minimata Bay. Bottom: prenatally exposed child

[1] While other types of bacteria may methylate mercury, only SRBs are considered in this paper.

and so may be areas of enhanced methylation. This is of concern in that estuaries are biologically productive zones that drain to coastal areas, so that methylmercury produced in estuaries may impact both estuarine and coastal biota. Estuaries are dynamic systems, with conditions such as salinity, sulfide, sulfate, organic matter (OM), and sedimentation changing on a tidal cycle, and both chemical factors (sulfate, sulfide, salinity, OM, metals, ligands) and physical factors (sediment fluxes, pH, temperature, bioturbation, sediment type, sediment grain size, tidal flushing) need to be examined in reference to mercury methylation.

Conditions that support SRB growth

Predicting methylation potential is complex in that it involves assessing SRB growth and mercury speciation, and some factors such as OM influence both. Very generally, SRBs flourish under high levels of sulfate that provide them with an electron acceptor, and under reducing conditions that limit microbial competition. They are also susceptible to temperature, with a Q10 of 3 (population triples for every 10C increase in temperature), and thus activity changes with seasons in shallow aquatic systems. Optimal sulfate concentrations have been reported at 0.2 to 0.5 mM, however, methylation can occur under higher sulfate conditions as long as sulfide concentrations are not too high (Langer et al 2001); sulfide can be removed either biotically by sulfide oxidizers are abiotically as a ligand to Hg(II). Under marine and estuary conditions, it has been estimated that SRBs degrade twelve times more organic matter than aerobic respirers and denitrifiers combined (Compeau and Bartha 1987). However, the soluble sulfide waste of SRBs may build up in anoxic sediments if a removal venue, such as sulfide oxidizing bacteria, is not in place. There is a window in which sulfate and sulfide are balanced in concentrations that allow for maximal SRB activity and therefore maximal mercury methylation (Figure 3).

Cells require both electron acceptors and electron donors. Although SRBs are limited in the organic matter they are able to use as donors (small alcohols and small fatty acids), studies consistently show a strong correlation between abundance of organic matter and SRB growth (Lambertson and Nilsson 2006; Stoichev et al 2004; Macalady et al 2000; Barkay et al 1997). The only study reviewed here that showed higher methylation rates in a sandy, low OM sediment vs a high OM muddy sediment was in the Barn Island Salt Marsh off the Connecticut River (Langer et al 2001), but it should be noted that there was extreme variation in methylation rates (11 to 1120 pmol MeHg/m^2/day) over very small (10 cm) horizontal distances in this location as compared to other locations sampled in the estuary. The authors noted that the unexpected high rates of methylation in the sandy area could also be due to high demethylation in high OM areas, such that the net methylation was lower in high OM areas.

In estuaries, fresh OM arrives consistently with high tides (Langer et al 2001). In a study done in a pristine estuary in Finland, although sulfide influenced methylation, organic matter was found to be the controlling factor and the best predictor of methylation (Lambertson and Nilsson 2006). In this location at the Bay of Bothnia, areas of low organic matter (0.04% OM) such as sandy bottoms had [MeHg] of about 1.6 ng/g dw, while areas where organic matter had accumulated (13% OM) had [MeHg] of about 4.2 ng/g dw, and up to 13 ng/g dw. There was a correlation with season as well, with higher OM available in the fall.

High OM found in deep, still areas of the bay would be used rapidly by heterotrophs, which would consume oxygen and create an anoxic environment, improving conditions for SRB growth (Stoichev et al 2004; Barkay et al 1997; Compeau and Bartha 1987). In addition, heterotrophs would be expected to break down OM into small carbon chains, some of which would reach SRBs, again improving conditions for them. Therefore, the impact of higher OM is to drive increased SRB activity, which then drives increased methylation. In contrast, when OM content was low as in a sandy area, oxygen went deeper into the sediment, so electron donors such as O_2, Fe(III), and Mn(IV) would be present, allowing non-SRB bacteria to flourish (Lambertson and Nilsson 2006). With SRBs driven deeper, and less OM available, less methylation occurred. Organic matter, then, could explain differences in the rate and depth of methylation horizontally across the bay (sandy vs still bottoms with accumulation of material), and differences seen over time (seasonal input of fresh phytoplankton and bacteria sedimenting to the bottom). A study looking at methylmercury in beaver-generated wetlands in New York also found that, while Hg_{TOT} did not follow the seasonal variations of OM fluxes, MeHg did (Driscoll et al 1998).

While the Finnish study observed higher MeHg in the fall with OM, a study in Spain correlated higher MeHg in the fall with warmer temperatures and higher SRB activity (Stoichev et al 2004). In contrast, the Barn Island salt marsh study found higher rates of methylation in the spring, decreasing in the fall. This may be due to the higher concentrations of sulfide in this area, with 50-80 uM of sulfide in May -- well into the area where methylation should be partly inhibited through formation of charged species (see "Sulfide" discussion below) -- and up to 3 mM in September, high enough to potentially inhibit SRBs themselves. This highlights how complex the controlling variables are. Another complication is the influence of OM as a ligand for Hg, in addition to its influence on SRB growth. Driscoll et al (1998) found in a study in the Andirondacks that organic acids produced in wetlands complexed both Hg(II) and MeHg, making Hg less bioavailable. This interaction may be essentially a competition between sulfide thiols on OM and Cl^- ions in brackish water (Benoit et al 2000), and is discussed in the section "Chloride" below.

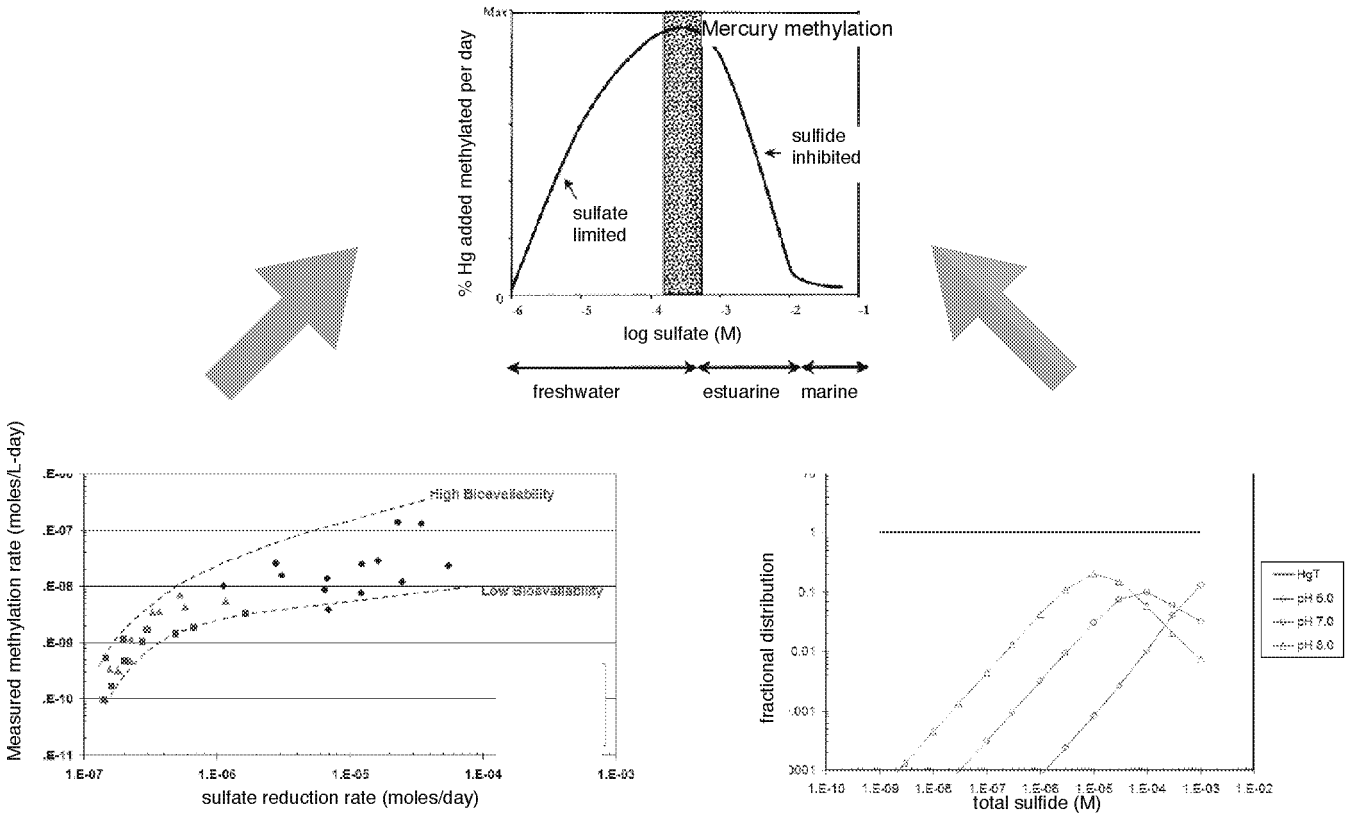

Figure 3. Relationship of sulfate and sulfides to methylmercury production. Top figure: at low sulfate levels, SRB activity is limited; as growth increases and sulfide waste accumulates, SRB activity also decreases (from Langer et al 2001). Left figure: Sulfate reduction rates correlate with MeHg production rates, indicating SRBs as the responsible group (Santore 2005). Right figure: When there are low levels of sulfide, no neutral, bioavailable HgS is formed; at high levels, charged species form, which also are not bioavailable (Santore 2005).

Conditions that provide neutral Hg species

In order for biotic methylation to occur, mercury species must be in an uncharged form that can cross cell membranes. While $HgCl_2$ has been postulated as the dominant neutral form in estuaries, the presence of $Hg(OH)_2$ and neutral mercury-sulfide species must also be considered. The issue of competing ligands is complex. Consider the following general molecules:

$$(CH_3 -- Hg -- L)^0 \qquad (Hg -- L_n)^0$$

Dissolved molecules may compete with mercury for the methyl group or with mercury for the ligand, and ligands may attach to mercury to form charged species. Ligands that compete to attach to Hg(II) are OH^-, Cl^-, S^{2-}, S_n^{2-}, thiol groups on OM, and Fe-S groups. Chloride ion is of significance in that the concentration of chloride will change with tidal influence (high tide bringing in more chloride, freshwater inputs diluting chloride during low tides), with the distance of the sediment from the mouth of the bay (more chloride at the mouth, less interior), and over season (less freshwater in dry seasons). Sulfide, on the other hand, is an influence in pore waters where SRB activity is producing H_2S, HS^-, and S^{2-} ions, with ion dominance determined by pH.

Sulfide

Neutral mercury-sulfide complexes could include $HgS^0_{(aq)}$, $Hg(HS)_2$, and $Hg(S_n)_2$ (polysulfide complex). One study compared mineral sediment from the estuary of the Patuxent River in Maryland with peat sediment from the Everglades (Benoit et al 1999). In both, [MeHg] decreased with increasing sulfide, and the dominant sulfide complexes were $HgS^0_{(aq)}$ and $HgHS_2^-$. The neutral form decreases with increasing sulfide as more $HgHS_2^-$ forms (Figure 4). In peat sediments, there was no relation between sulfide and Hg(II), but a distinct trend of decreasing MeHg with increasing sulfide; [MeHg] was 3 ng/g dw when pore water sulfide was 0.1uM, decreasing to near

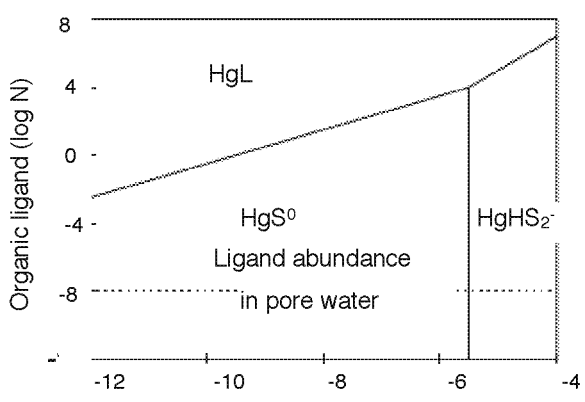

Figure 4. Speciation of dissolved Hg(II) with changing sulfide concentrations; data from sediment pore waters of Long Island Sound at pH 8 (Hammerschmidt et al 2004)

zero when sulfide increased to 100 uM. In mineral sediment, increased sulfide correlated with increasing Hg(II) and decreased MeHg; [MeHg] was 0.8 ng/g dw at 0.1 uM sulfide and near zero at sulfide as low as 1 uM, remaining near zero to 100 uM sulfide.

As in the above, in the Bothnian Bay study concentrations of pore water sulfide correlated statistically with methylation rates (Barkay et al 1997). Experimentally, sulfide levels of 1 uM enhanced mercury methylation, but increasing sulfide from 1 uM to 5 uM decreased methylation by 20%. Significant decreases did not occur until greater than 5 - 10 uM, with 90% decrease seen at 350 uM (Benoit et al 1999). In Bothnian Bay, pore water sulfide was 2 - 20 uM, Hg_{TOT} ranged from 20 to 120 ng/g dw, despite being a pristine area, and MeHg was 0.1 to 13 ng/g dw, for a ratio of 4 - 13% MeHg, much higher than reported for some polluted areas (Heyes et al 2004; Stoichev et al 2004). It is not expected that sulfide will inhibit SRBs themselves until the mM range, therefore speciation may affect methylation more than sulfide toxicity.

Polysulfides may also form neutral complexes with Hg. Polysulfides form when there are high levels of sulfides and $S(II)_{TOT}$ should include H_2S, HS^-, S^{2-}, S_3^{2-}, S_4^{2-}, S_5^{2-}, S_6^{2-}, HS_4^-, and HS_5^-; that is, polysulfide chains with one sulfur atom in oxidation state -2. If elemental sulfur is present in the system (to allow the formation of polysulfides), then most dissolved mercury appears to be bound in polysulfide complexes. When using a speciation model to predict levels of dissolved mercury, including $Hg(S_x)^{2-}$ improved the fit of the model, and including HgS_xOH^- in addition to the polysulfide complexes gave a slightly better fit. Considering HgS_xH^- did not improve predictions, suggesting that this species is not important.

Gun et al, while investigating Lake Kinneret in Israel, found polysulfides and polysulfanes (H_2S_n) forming even in an oxygen-rich environment, as long as organosulfur compounds such as methionine were present (Gun et al 2000). The chloride concentration was high at 225 mg/L (6mM), and sulfate was optimal for SRB growth at 52 mg/L (0.5 mM). The potential impact of polysulfides on mercury methylation was not investigated, as the authors were studying the formation of dimethyl disulfides.

Sulfides may also increase the solubility of $HgS_{(s)}$ (cinnabar). Jay et al looked at the polysulfides that may form from the reaction of HgS with HS^- (Table 3). Experimentally, Jay et al found polysulfides increase the solubility of cinnabar, especially at high pH (around 8).

If neutral polysulfide - mercury complexes form, how bioavailable are they? Jay et al looked at the bioavailablity of mercury under varying $[S^{2-}]$ when mercury was or was not complexed with polysulfides. To find the total K_{ow} of mercury species, they used the equation

$$Dow = \sum_i K_{ow,i}\, \chi_i \qquad (1)$$

for i = species and χ_i the mole fraction of that species in the total mercury species, and found D_{ow} decreased with increasing $[S^{2-}]$ for polysulfide complexes, and polysulfide complexes with mercury had higher K_{ow} than mercury complexes without (Table 4).

Table 3. Stability constants of some mercury-sulfide interactions at ionic strength of 0.5M (from Jay et al 2000)

Formation reaction	log K	original reference
$HgS_{(s)} + HS^- = HgS_2^{2-} + H^+$	-13.0	Benoit et al 1999
$HgS_{(s)} + HS^- = HgS_2H^-$	-4.5	Benoit et al 1999
$HgS_{(s)} + HS^- + H^+ = Hg(SH)_2$	+1.0	Benoit et al 1999
$HgS_{(s)} + H^+ = HgSH^+$	-16.8	Dyrssen and Wedborg 1991
$HgS_{(s)} = Hg^{2+} + S^{2-}$	-53.5	Benoit et al 1991
$HgS_{(s)} = HgS_{(aq)}$	-9.3	Dryssen and Wedbor 1991

While intriguing, most estuary sediment pore water contains sulfide concentrations less than 1 mM, although some are as high as 3 mM seasonally (Langer et al 2001). It is also questionable whether large mercury-polysulfide complexes would be able to diffuse passively across cell membranes, despite a higher K_{ow}; and the experiment indicates that at sulfide concentrations more likely to be encountered in estuaries, the D_{ow} is essentially the same for Hg complexed with polysulfides or not.

Table 4. Octanol water partitioning for sum mercury species when polysulfides form or not (Jay et al 2000)

$[S^{2-}]$ (mM)	D_{ow} for Hg with S(0) present	D_{ow} for Hg without S(0) present
5	4.5	3.5
0.4	1.5	1.0
0.05	<0.5	nd

Chloride/Salinity

Chloride, like sulfide, affects K_{ow}. The concentration of $HgCl_2$ has a greater influence on the K_{ow} of the sum mercury species than the concentration of Hg-OM in a study in the Everglades (Benoit et al 1999). When this was explored further, it was determined that the part of OM that Hg(II) was binding to was most likely a thiol group. For mercury-complexed species i being $HgCl_2$, $HgCl_3^-$, and Hg-DOM, Benoit described the equation

$$D_{ow} = 3.3[HgCl_2] + 0.1\,[Hg\text{-}OM] \quad (2)$$

with the assumption that the K_{ow} of $HgCl_3^-$ is essentially zero. Sample stability constants indicated that OM was forming stable 1:1 complexes with mercury, and that mercury was most likely binding to thiol functional group on the DOM. The complex 2SH:1 Hg had a log K_s of 41.6, while 1SH:1Hg had a log K_s of 12.8. The general hypothesized reaction is

$$Hg^{2+} + RSH^{n-} = HgRS^{(n-1)-} + H^+ \quad (3)$$

Therefore, the influence of OM with relation to dissolved mercury is to some degree a matter of competition between -SH groups on the OM with S^{2-} and HS^- from sulfate reduction activities.

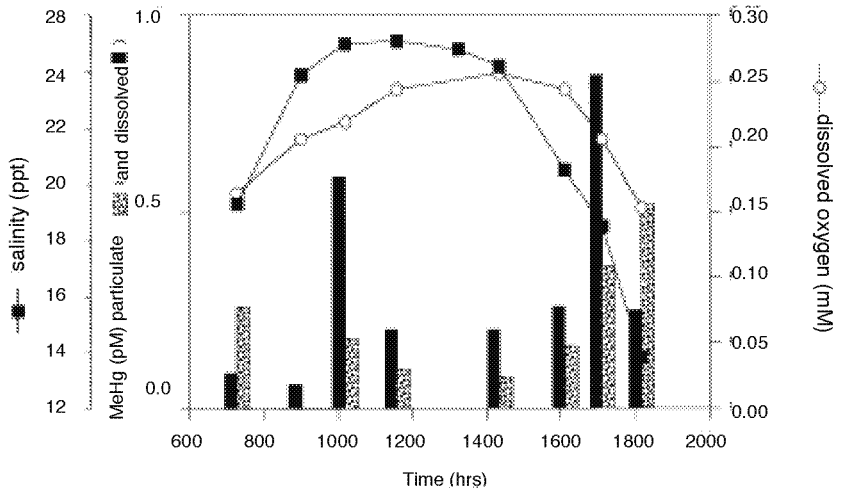

Figure 5. As salinity and dissolved oxygen increase with high tide (noon), mercury methylation decreases at Barn Island marsh, an estuary (Langer et al 2001)

The formation of the neutral $HgCl_2$ group is dependent on OM and pH (Benoit et al 1999). The percent of Hg_{TOT} that was $HgCl_2$ was greatest at $[Cl^-] = 10^{-2}$ and decreased in a classic bell curve to zero at 1M and at 10^{-5}M. The dominant complex at 0.5M, the chloride concentration of seawater, however, is $HgCl_3^-$, a charged species (Barkay et al 1997). Therefore the effect of chloride on neutral mercury species could be significant, and it is likely that estuaries will vary in methylation activity over time (with tides, Figure 5) and space (near or far from ocean boundary) due solely to chloride. Water pH also influences whether the neutral $HgCl_2$ molecule will be available for SRBs: the [Hg-OM]: $[HgCl_2]$ ratio decreased by a factor of 10 for every pH unit increase, that is, as waters become more alkaline, Hg(II) is more likely to bind to Cl^- ion than to organic material. Together this information tells us that maximum methylation would be expected to occur when pH is alkaline and the water is weakly brackish.

Demethylation

Neither organic matter nor sulfide affected rates of demethylation in the Finnish study (Lambertson and Nilsson 2006), although Langer suggested that OM increased demethylation in the Barn Island salt marsh. In Bothnian Bay, demethylation remained consistent over depth, despite a changing microbial community, indicating that the process was abiotic, or that many types of bacteria were participating in demethylation processes. Bacteria demethylate mercury through reduction or oxidation (Oremland et al 1995); SRBs, methanogens, and other anaerobes (potentially denitrifiers and Fe(III) and Mn(IV) reducers) demethylate in freshwater (Oremland et al 1995), but only SRBs demethylate in estuaries (Martin-Doimeadios et al 2004). It is possible to discriminate between abiotic and biotic demethylation by radioisotope tracers, in that spiking with ^{201}MeHg will provide a rate constant for the degradation of MeHg in aqueous form (abiotic degradation), and spiking with ^{199}MeHg will give the rate constant for degradation of MeHg in the cell (Martin-Doimeadios 2004).

Placid vs Dynamic estuary systems

The impact of controlling factors such as sulfide, sulfate, pH and so forth need to also be looked at in the context of water/sediment interaction. The dynamics of a placid system, in which organic material accumulates on a still bottom, forming an anoxic zone and a redox transition zone is different from an estuary system that is subjected to strong diurnal and seasonal tidal flooding. Studies done on the Hudson River found that a substantial amount of sediment was moved out of the estuary each spring during flooding events, but most returned over the course of the year through "tidal sloshing".

In placid estuaries with redox transition sediments, such as Barn Island salt marsh in Connecticut or the Everglades, the area in which SRBs are active is often a strongly defined narrow depth of sediment, often beginning a few centimeters below the surface and extending down several centimeters until either OM becomes limiting or sulfide limits methylation. In addition, methylmercury made in sediment porewater may be prevented from reaching the overlying bulk water, as it must travel through an "oxic zone" near the surface that oxidizes neutral species to charged species that are not bioavailable (Gagnon et al 1996). However, Langer et al found that the redox transition zone migrates diurnally, with photosynthesis in the day and high sulfide at night, so that there is no permanent oxic layer and methylmercury can in fact diffuse to overlying water (Langer et al 2001).

Transport of methylmercury out of sediment involves a combination of diffusion (concentration gradient), bioturbation, tidal effects, and sediment suspension by waves or currents.

In areas with strong sediment suspension, the methylation zone may actually be larger, extending from the surface down (Hammerschmidt et al 2004; Sunderland et al 2004). This is counter-intuitive, as areas in which there is enough turbulence to cause sediment suspension would be expected to be highly aerated. While wave-induced suspension was examined, bioturbation was a main focus. Bioturbation refers to the disturbing of sediment by benthic infauna. This activity in Long Island Sound disturbed sequestered "legacy" mercury, working the mercury pools down into deeper sediments, transporting OM deeper, and appeared to remove some sulfide. The overall effect was to create a larger zone favorable to SRBs. As with previous studies, there was a strong correlation with OM. Some mercury was associated with Fe complexes, assumed to be iron hydroxides, and the redox cycle of iron strongly affected MeHg partitioning onto particles and mobility.

In the Canadian Bay of Fundy, mercury methylation was found to 15 cm depth. As with the Long Island study, this was due to deep mixing and disturbance of legacy mercury pools, although in the Bay of Fundy the mixing was probably due to very strong tides (Sunderland et al 2004). Again, resuspension of particles did not significantly affect methylmercury transport, but turbulence did transport mercury and carbon deeper into sediment, forming anoxic organic rich "pockets" or "mottles" to make a more favorable region for SRBs and cause a deeper methylation zone (Figure 6). In addition, rapid cycling of mercury was seen at the sediment-water interface. With methylation occurring all the way to the surface, and no "oxic zone" for scavenging reduced mercury species, methylmercury could easily cross from porewater into the overlying bulk water, and from there into coastal zones (Sunderland et al 2004).

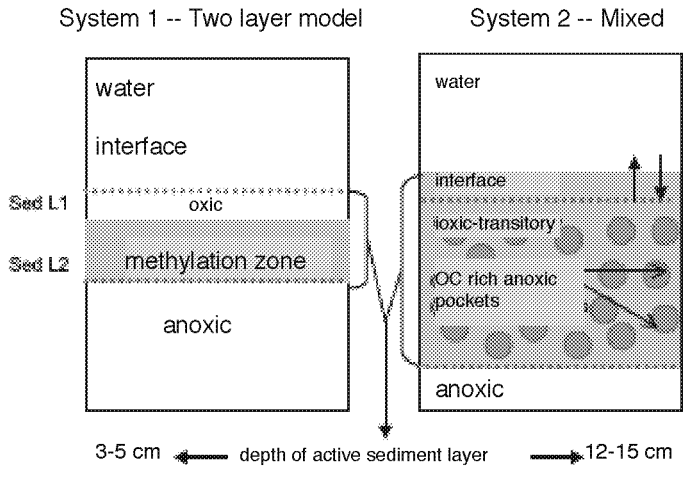

Figure 6. Conceptual model of mercury speciation in depositional vs well-mixed sediments (Sunderland et al 2004)

Transport via sediment -- will methylmercury made in an estuary move to coastal areas?

In the study done by Driscoll et al regarding riparian wetlands and wetlands created by beaver dams, transport of both Hg_{TOT} and MeHg were linked to OM (Driscoll et al 1998). This was not further explored to see whether the relationship was co-incident, with flood waters moving both OM and soluble $HgCl_2$ with the two not necessarily related, or whether species of mercury were actually attached to OM particles. A study done in Spain, did look at the physical transport of methylmercury by sediment, and compared the Seine River estuary to the Adour River estuary on the Bay of Biscay (Stoichev et al 2004). Fine-grained mercury-contaminated particles were "pushed" from the estuary into coastal waters through a bottleneck at the head of the Adour estuary that caused seasonal floodwaters to increase in velocity as they were leaving, and carried fine particles along. The Seine, however, did not have a narrow opening, and particles settled prior to reaching coastal areas. However, the potential impact of more point sources near the Adour could not be ruled out as a source of methylmercury to the coast. In a study of the Hudson River and Long Island Sound (Heyes et al 2004), there is significant "sloshing" of sediment, with 100,000 to 500,000 tons of sediment moved out of the river and estuary in the spring, and most returning over the course of the year. Re-suspension of sediment appears to have only a minor impact, in that Hg(II) and MeHg that are attached to sediment are not released during resuspension. However, the fact that so much sediment moves out of the river/estuary areas and into the harbor implies the potential for transport of MeHg into coastal areas.

Summary

Estuaries methylation rates change over time, space, and depth. Over time they change with daily cycles--decreasing as rising tides increase salinity, which increases chloride concentration and shifts Hg-Cl species from neutral $HgCl_2$ to charged species-- and with seasons, due both to changing temperatures, favoring methylation during warm seasons, and to changing amounts of organic matter as phytoplankton die and sediment out in fall. They change over space, with different bottom types strongly affect methylation rates due to the amount of organic matter available and the reducing conditions and with less methylation at high salinity areas near the estuary mouth. Methylation changes over depth in still waters, with greater reducing conditions at depth favoring

methylation until sulfide levels are high enough to shift dominance of the neutral sulfide (and possibly polysulfide) mercury species to charged species.

In addition, if legacy pools of mercury are present, burrowing infauna may work the mercury deep into sediment, increasing the overall area that methylation may occur in. Coastal fauna may be impacted through methylation reaching to the overlying bulk water via diurnal elimination of the oxic zone at night or benthic infauna activities. Although sediment transport occurs with tidal flushing or seasonal flood events, especially if the estuary narrows at the mouth allowing fine-grained particles to flush into coastal areas, this transport may not release MeHg from particles.

Modeling and predicting mercury methylation is made difficult by due to competition between chloride, sulfide, polysulfide, and organic matter thiol groups as potential ligands for mercury -- especially with changing ion conditions over time, depth, and space -- and the competition between methylators and demethylators for organic matter. Organic matter may be the best predictor of methylation, but levels of chloride and sulfide will moderate OM influences through the formation of bioavailable neutral species or charged species. In conclusion, it remains necessary to decrease atmospheric mercury levels, the primary source of mercury to pristine areas, but due to the cycling of mercury species, it is unlikely that methylmercury in fish tissues will decrease in either polluted or pristine areas soon.

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